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Effect of physical pretreatment on dilute acid hydrolysis of water hyacinth (*Eichhornia crassipes*)

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ABSTRACT

Effects of different physical pretreatments on water hyacinth for dilute acid hydrolysis process (121 ± 3 °C, 5% H_2SO_4, 60 min) were comparatively investigated. Untreated sample had produced 24.69 mg sugar/g dry matter. Steaming (121 ± 3 °C) and boiling (100 ± 3 °C) for 30 min had provided 35.9% and 52.4% higher sugar yield than untreated sample, respectively. The highest sugar yield (132.96 mg sugar/g dry matter) in ultrasonication was obtained at 20 min irradiation using 100% power. The highest sugar production (155.13 mg sugar/g dry matter) was obtained from pulverized samples. Hydrolysis time was reduced when using samples pretreated by drying, mechanical comminution and ultrasonication. In most methods, prolonging the pretreatment period was ineffective and led to sugar degradations. Morphology inspection and thermal analysis had provided evidences of structure disruption that led to higher sugar recovery in hydrolysis process.

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1. Introduction

Invasive land and aquatic weeds (switchgrass, Bermuda grass, water hyacinth, and water lettuce) are some potential lignocellulosic materials that have been studied for bioethanol production (Sun and Cheng, 2002; Mishima et al., 2008). In most countries, water hyacinth (*Eichhornia crassipes*) is recognized as a big threat to agriculture, water mitigation and aquatic ecosystem owing to its rapid growth rate and robust nature (Mathur and Singh, 2004). Water hyacinth has high percentage of cellulose and hemicellulose (44–66.9% of dry weight basis) and low lignin content (Gunnarsson and Petersen, 2007; Nigam, 2002). Table 1 summarizes the cellulose, hemicellulose and lignin content of water hyacinth according to some published literatures and from this study. The estimated annual biomass production of water hyacinth is around 90–140 ton dry matter per hectare area depending on geographical and climate factor (Gunnarsson and Petersen, 2007; Nigam, 2002).

One of major hurdles in production of bioethanol from lignocellulosic material is low solubilization of cellulose and hemicellulose during hydrolysis process to produce sugar. In lignocellulosic material, the celluloses, hemicelluloses and lignin are linked and formed a strong structure which is difficult to be processed in raw condition (Boudet et al., 2003). Thus, pretreatment is required in order to render those components for further exploitations. Biomass pretreatment method can be classified into different categories, e.g. physical, chemical, biological, and combination of these methods (Silverstein et al., 2007). Physical pretreatment alters the structure of biomass by applying mechanical stress without addition of chemical or biological reagent. The pretreatment process will increase the active surface area and pore sizes of the biomass (da Costa Sousa et al., 2009). The efficiency in the later process is also contributed by the ability of pretreatment process to reduce the degree of crystallinity and polymerization of cellulose and hemicellulose (Binod et al., 2010; Silverstein et al., 2007).

Mechanical comminution (size reduction) of wet or dry lignocellulosic materials can be achieved by single or combined milling, grinding, and chipping (Alvira et al., 2010). Several studies on the effect of particle sizes on biomass processing have concluded that the improvements in the studied process is associated to the ability of pretreatment to provide larger active surface area and reduction of crystallinity of the materials (Sun and Cheng, 2002). Steaming and boiling are pretreatment processes where samples are being retained in water/steam under elevated temperature and pressure. Steaming pretreatment is optionally accompanied with decompression at the end of process (also known as steam explosion) and either with or without catalyst (Balat et al., 2008). Ultrasonication pretreatment refers to application of ultrasonic waves (18–20 kHz) to substrates which are suspended in liquid medium. The enhancement is regarded to alteration of biomass structure induced by cavitations and/or size reduction due to interparticle collision and cavitations that occurs during ultrasonication (Yu et al., 2009).

In this work, effect of different type of physical pretreatments on water hyacinth for dilute acid hydrolysis was studied. The

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Table 1
Lignocellulosic components of water hyacinth.

Component (% dry matter)			References
Hemicellulose	Cellulose	Lignin	
33.4	19.5	9.27	Gunnarsson and Petersen (2007)
22	31	7	
33.97	18.0	26.36	
43.4	17.8	7.8	
18.42	25.61	9.93	
48.7	18.2	3.5	Nigam (2002)
27.1	19.7	NA[a]	Mishima et al. (2008)
46.7[b]		27.7	Girisuta et al. (2008)
40.2[b]		6.5	This study

[a] Not available.

[b] The value represents total amount of hemicellulose and cellulose.

selected physical pretreatment method in this study includes mechanical comminution (grinding), drying, boiling, steaming, ultrasonication and combination. These are the common physical pretreatment methods applied to lignocellulosic material (Binod et al., 2010). The morphology of samples before and after the pretreatment process, the amount of sugar produced from dilute acid hydrolysis of water hyacinth's samples and thermal analysis of raw and pretreated water hyacinth samples were recorded and evaluated accordingly.

2. Methods

2.1. Raw material

Fresh water hyacinth plants were harvested from local water bodies in Serdang, Selangor, Malaysia. Extensive roots and rotten parts of the plants were discarded. Water hyacinth's root has a very high ash content (∼50% dry matter) which is enriched with heavy metal and its lignin content was also higher compared to the stem and leaf (Cheng et al., 2010). Since these might affect the overall experimental results, the root of the plant is not tested.

The plants were cleaned thoroughly with tap water to remove adhering dirt and then cut into 2–3 cm length. For preparation of dried sample, the plant was oven-dried for two to three days at 60 ± 3 °C until complete drying attained. Samples were spread properly on several drying pans and were ensured not stacking to guarantee a complete drying. For wet samples, freshly collected plants were used.

2.2. Chemical reagents

All chemical reagents used in this study were of analytical grade. Concentrated sulphuric acid (98% wt) was purchased from Fisher Chemicals. Sugar monomers (glucose, galactose, mannose, xylose and arabinose) for standards were purchased from Sigma–Aldrich and Acros Organics.

2.3. Characterization of water hyacinth

Water hyacinth plants were tested for its chemical composition (hemicellulose, cellulose, lignin, ash) using thermogravimetric analysis (Girisuta et al., 2008; Negro et al., 2003). 5 mg of water hyacinth samples were pyrolyzed in nitrogen atmosphere at temperature 25 until 800 °C, with increment of 10 °C/min. The generated weight loss vs. temperature curve was then examined to determine the water hyacinth's chemical compound based on the degradation of individual components at specified temperature range (Haykiri-Acma et al., 2010; Yang et al., 2007). Hemicellulose, cellulose and lignin content of water hyacinth sample used in this experiment are listed in Table 1.

To determine the water hyacinth's moisture content, as well as to find out the total solid content in this biomass, initially-weighed water hyacinth sample was oven dried (105 ± 3 °C) and consecutively weighed until no further weight losses were detected (Sluiter et al., 2005). The recorded total weight loss was taken as the moisture content of the sample, while the remnant is the total solid in the biomass. From moisture content analysis, it has been found that the water hyacinth sample used in this works contains 96.6% moisture, similar to that reported in other studies, in range of 95–97% (Girisuta et al., 2008; Nigam, 2002). This value was used to estimate the amount of total dry matter in wet samples.

2.4. Pretreatment of water hyacinth

For pretreatment, water hyacinth samples were either dried, ground, boiled, steamed, sonicated and/or combination of these methods. Table 2 provides the summary of pretreatment condition for all samples. For pretreatment processes that involve submerging water hyacinth sample in water, i.e. boiling and ultrasonication, the solid (total weight)–liquid ratio was fixed at 1:10.

For preparation of dried samples (Sample 2 and 4), water hyacinth samples of 2–3 cm length were placed properly on drying pans (not stacking nor closely packed) before being oven dried at 60 ± 3 °C for two to three days. Samples were consecutively weighed until constant weight is attained. The dried samples were either straightly used for experiments or transferred into airtight containers until further use.

On pretreatment by means of reducing the biomass size, grinding method was selected. Laboratory mill was used to grind Samples 3 and 4. The mill's components were cleaned thoroughly and allowed to dry before each preparation cycle. These samples were then screened through a 2.80 mm wire-mesh sieve (Aimil Ltd., India).

Samples 5x and 6x were prepared by boiling and steaming raw water hyacinth sample, respectively. Boiling process was carried out at 100 ± 3 °C in atmospheric pressure for 90 min. 100 g of fresh water hyacinth sample was loaded in glass beakers filled with 1000 ml of distilled water. The beakers were then submerged in a water bath set at boiling temperature. Samples were withdrawn from the beaker at every 30 min interval to investigate the effect of boiling time.

Non-catalyzed steaming process for samples 6x were conducted at 121 ± 3 °C in an autoclave with no final decompression took place. Samples were placed on wire-mesh container to allow thorough steaming on the samples. Since the steaming process is conducted in a closed reactor where interruption for withdrawing sample is not possible, three steaming cycles were carried out at three different retention time, namely 30, 60 and 90 min. 20 g of fresh water hyacinth sample was used in each cycle.

After boiling and steaming pretreatment, the samples were cooled down to room temperature. All excess water was drain prior to hydrolysis process. The draining process is carried out by spreading the sample on wire-mesh container before being place on absorbing paper to remove all the excess water from the pretreatment processes.

For preparation of ultrasonicated samples (Sample 7x–11x), a 13 mm ultrasonic probe coupled to ultrasonic processor with a resonance capacity of 20 ± 50 kHz (Cole Palmer, USA) was used. 100 g of fresh water hyacinth sample was loaded in glass beaker (diameter 10 cm, height 16 cm) containing 1000 ml distilled water. The ultrasonicator probe was submerged in the beaker at maximum (but not touching the bottom of the beaker) to ensure uniform irradiations on the sample and have direct contact with the mixture inside the beaker. The ultrasonication pretreatment processes were carried out at different ultrasonicator power of 20%, 40%, 60%, 80% and 100%, each for 30 min. During the 30 min of irradiation

Table 2
Pretreatment process introduced to samples before hydrolysis.

Samples	Condition	Pretreatment
1	Wet	Untreated
2	Dry	Oven dried
3	Wet	Pureed
4	Dry	Oven dried, powdered
5A,B,C	Wet	Boiled at 100 ± 3 °C for 30, 60, and 90 min, respectively
6A,B,C	Wet	Steamed at 121 ± 3 °C for 30, 60, and 90 min, respectively
7A,B,C	Wet	Ultrasonicated at 20% ultrasonicator power for 10, 20 and 30 min, respectively
8A,B,C	Wet	Ultrasonicated at 40% ultrasonicator power for 10, 20 and 30 min, respectively
9A,B,C	Wet	Ultrasonicated at 60% ultrasonicator power for 10, 20 and 30 min, respectively
10A,B,C	Wet	Ultrasonicated at 80% ultrasonicator power for 10, 20 and 30 min, respectively
11A,B,C	Wet	Ultrasonicated at 100% ultrasonicator power for 10, 20 and 30 min, respectively

process, sample was withdrawn at every 10 min to investigate the effect of irradiation time. The temperature of the mixture during the irradiation process was controlled at 30 ± 3 °C.

2.5. Dilute acid hydrolysis of water hyacinth

Water hyacinth samples (1–5 g) were hydrolyzed in 50 ml of 5% sulphuric acid solution at 121 ± 3 °C in TOMY-SEIKO SX-700 autoclave (Tomy-Seiko, Japan). The process was conducted for 60 min. The water hyacinth sample–sulphuric acid solution ratio was kept below 10% (w dry matter/v). All experimental runs were repeated to ensure reliability of the data and results' reproducibility. The hydrolysate liquor was then diluted and filtered through 0.2 mm syringe filter prior to sugar analysis.

2.6. Reducing sugar estimation and sugar yield

The composition of hydrolysate liquor was measured using High Performance Liquid Chromatography (HPLC) adapting procedures outlined by Sluiter et al. (2006). The HPLC system was equipped with Phenomenex Rezex RCM Monosaccharide Model 00H-0130-K0 column which is able to detect glucose, xylose, arabinose, mannose, galactose and cellobiose. Filtered deionised distilled water was used as mobile phase at flow rate of 0.6 ml/min. Column heater was set at 85 °C. The column was calibrated with analytical grade sugar monomer sample prepared at different concentrations, i.e. 5, 10, 30 and 50 mg/ml. Yield of sugar from dilute acid hydrolysis of water hyacinth was reported in total sugar release divided by the total dry matter of samples (mg sugar/g dry matter).

2.7. Morphology of samples

The morphologies of samples before and after the pretreatment process were observed under light microscope (Leica Microsystems, Germany). The inspections were performed under various magnifications, i.e. 100×, 400×, 1000×, until clear images obtained. Images of specimen were captured using KY-F55BE JVC color video camera (JVC, Japan) attached to the microscope.

2.8. Thermal analysis

Thermogravimetric analysis (TGA) method was employed in examining the thermal degradation behavior of water hyacinth sample. Biomass components will experience fractional decomposition at certain temperature range during the pyrolysis. Approximately 5–10 mg of selected water hyacinth samples were pyrolyzed at temperature increment rate of 10 °C/min using Mettler–Toledo TGA/SDTA851^e (Mettler–Toledo, Switzerland) TGA unit. The pyrolysis was carried out in nitrogen atmosphere, supplied at a rate of 40 ml/min in order to diminish oxidation effects on the sample.

3. Result and discussion

3.1. Effect of pretreatment on reducing sugar yield from dilute acid hydrolysis

The liquid phase of the hydrolyzed product was obtained and analyzed using HPLC to estimate its reducing sugar content. The brown liquor comprised predominantly of xylose, glucose and arabinose with traces of galactose and mannose, similar to other works in acid catalyzed hydrolysis of water hyacinth (Girisuta et al., 2008; Nigam, 2002). Table 3 shows the amount of reducing sugar in individual monomer obtained after 60 min hydrolysis of all samples. Higher cumulative amount of C5 sugar (pentoses) than C6 sugar (hexoses) is closely related to higher hemicellulose content compared to cellulose in water hyacinth biomass as listed in Table 1.

For untreated samples (Sample 1) and dried samples (Sample 2), the respective sugar yield was found to be 24.69 mg sugar/g dry matter and 111.4 mg sugar/g dry matter. High moisture content in untreated samples might be the dominant factor contributing to large difference in these results. The high yield from dry samples is mainly credited to high level of diffusivity of dried material and reduction of water content which had hindered further dilution of acid as it penetrates through the samples. In study of enzymatic hydrolysis of switchgrass, sugar production was decreasing when moisture content increases (Karunanithy and Muthukumarappan, 2010).

For grounded (size reduced) wet and dry samples (Samples 3 and 4), the sugar yield increased significantly to 59.32 mg sugar/g dry matter and 155.13 mg sugar/g dry matter compared to untreated sample, respectively. The increasing yield of sugar by 130% in Sample 3 has shown that size reduction has successfully overcome the effect of high moisture content as exhibited in hydrolysis of Sample 1. Other parallel studies also share the same findings where improvement on the hydrolysis outcome was contributed by substrate's size reduction (Dasari and Berson, 2007; Yeh et al., 2010). Production of sugar from dried samples (Sample 2 and 4) are also different when particle size of the samples was varied where higher sugar is obtained when particle size is reduced. Size reduction has enhanced the hydrolysis process because the surface area of samples was increased and thus improved acid penetration into the samples (Sun and Cheng, 2002).

Fig. 1 compares the total amount of reducing sugar from dilute acid hydrolysis of boiled and steamed water hyacinth samples (Samples 5x and 6x). Boiling and steaming pretreatment had produced higher sugar amount than untreated condition, up to 35.9% and 52.4%, respectively. Resulting shear stress and tensile forces from the pretreatment process will breakdown the substrate and subsequently increase the surface area and accessibility to cellulose (Chen et al., 2010). It is believed that the same mechanism was responsible for the improved sugar release from boiled and steamed samples in this work. Similar steaming method (121 °C at neutral pH) was found to improve COD solubilization of water hyacinth biomass for biomethanation process (Patel et al., 1993). However, this improvement may not be applicable for different types of feedstock because of the variation in their lignocellulosic contents and different process requirements (Rogalinski et al.,

Table 3
Total sugar yield after 60 min hydrolysis (121 ± 5 °C) of different pretreated samples.

Sample	Pretreatment	Sugar yield (mg sugar/g dry matter)					
		Glu	Gal	Man	Xyl	Ara	Total
1	Untreated	5.82	0.21	0.24	13.75	4.67	24.69
2	Oven dried	29.50	0.37	0.24	56.39	24.95	111.45
3	Pureed	17.97	0.42	0.37	31.72	8.84	59.32
4	Oven dried, powdered	47.42	1.25	1.17	73.87	31.42	155.13
5A	Boiled at 100 ± 3 °C for 30 min	7.84	0.21	0.24	20.96	4.30	33.55
5B	Boiled at 100 ± 3 °C for 60 min	6.72	0.14	0.09	12.71	5.19	24.85
5C	Boiled at 100 ± 3 °C for 90 min	6.21	0.09	0.05	11.68	2.79	20.82
6A	Steamed at 121 ± 3 °C for 30 min	8.51	0.33	0.33	22.70	5.75	37.62
6B	Steamed at 121 ± 3 °C for 60 min	8.82	0.23	0.28	13.74	5.14	28.21
6C	Steamed at 121 ± 3 °C for 90 min	7.60	0.35	0.24	8.98	5.57	22.74
7A	Ultrasonicated (20% power, 10 min)	9.06	0.81	0.45	16.13	6.55	33.00
7B	Ultrasonicated (20% power, 20 min)	14.34	1.02	0.88	22.48	8.50	47.22
7C	Ultrasonicated (20% power, 30 min)	14.07	1.17	1.10	21.66	10.80	48.80
8A	Ultrasonicated (40% power, 10 min)	9.73	0.79	0.65	19.64	7.93	38.74
8B	Ultrasonicated (40% power, 20 min)	19.10	1.88	1.42	31.71	16.17	70.28
8C	Ultrasonicated (40% power, 30 min)	23.66	2.06	1.46	34.46	16.03	77.67
9A	Ultrasonicated (60% power, 10 min)	19.21	1.79	1.88	27.13	16.11	66.12
9B	Ultrasonicated (60% power, 20 min)	25.74	2.08	1.54	33.19	16.56	79.11
9C	Ultrasonicated (60% power, 30 min)	27.79	1.97	1.93	35.52	16.92	84.13
10A	Ultrasonicated (80% power, 10 min)	23.41	1.67	1.63	30.90	14.54	72.15
10B	Ultrasonicated (80% power, 20 min)	27.80	1.86	1.78	58.64	26.44	116.52
10C	Ultrasonicated (80% power, 30 min)	28.60	2.12	1.98	42.64	21.91	97.25
11A	Ultrasonicated (100% power, 10 min)	27.67	1.90	1.92	34.50	16.57	82.56
11B	Ultrasonicated (100% power, 20 min)	35.62	1.93	1.86	60.45	33.10	132.96
11C	Ultrasonicated (100% power, 30 min)	29.37	1.69	1.87	52.34	22.28	107.55

2008). For example, Nlewem and Thrash (2010) found a negligible enhancement on enzymatic hydrolysis outcome when treating switchgrass with boiling water (100 °C) and recommended higher temperature to be used.

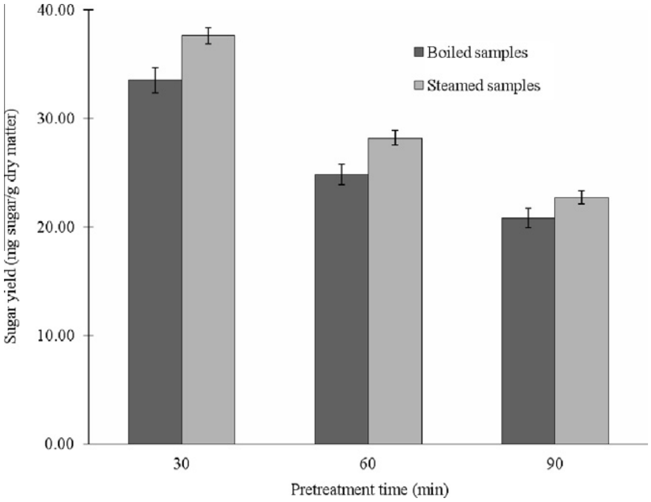

Fig. 1. Production of sugar (mg sugar/g dry matter) from dilute acid hydrolysis of boiled and steamed water hyacinth. Error bars represents standard error of experiments.

Prolonging pretreatment period in boiling and steaming pretreatments had reduced the amount of sugar yield. Liberation of natural acids from the feedstock and formation of organic acids during long retention period had amplified the acid concentration of the mixture; eventually leading to degradation of sugars into aldehydes, namely furfural and 5-HMF (Balat et al., 2008).

Ultrasonication pretreatment at different percent power and irradiation time had exhibited interesting results. Generally, yield of sugar from dilute acid hydrolysis of ultrasonicated samples (Sample 7x–11x) was comparatively higher than the raw sample, which is in good agreement with similar works dedicated in investigating effect of this pretreatment on hydrolysis performance of biomass (Sun and Tomkinson, 2002; Yu et al., 2009). The highest amount of sugar from hydrolysis of ultrasonicated sample, 132.96 mg sugar/g dry matter, was obtained from Sample 11B (ultrasonicated at 100% power for 20 min).

Fig. 2 shows the sugar yield from hydrolysis of water hyacinth samples ultrasonicated at different percent power for irradiation period of 10, 20 and 30 min. The sugar production from hydrolysis of ultrasonicated samples was found to be proportional to the intensification of ultrasonicator power used in the pretreatment process. Similar trend was observed in hydrolysis of ultrasonicated corncobs and palm oil empty fruit bunch (Wang and Zhang, 2006; Yunus et al., 2010).

In the effect of pretreatment time, for ultrasonication using low to medium percent power (20–60% power), the sugar release is increasing with the pretreatment period. However, irradiation at high percent power (80% and above) has shown different trend where the sugar yield has decreased when irradiation time was extended beyond 20 min. Prolonging the irradiation time at high power range did not provide improvement on sugar yield indicating maximum or optimum operating condition (Montalbo-Lomboy et al., 2010). Based on the hydrolysis outcome from all 15 different combinations of percent power and irradiation time, highest sugar yield (116.52–132.96 mg sugar/g dry matter) can be obtained by conducting pretreatment using 80–100% ultrasonicator power for 20 min.

3.2. Effect of pretreatment on hydrolysis processing time

Fig. 3 shows the total release of sugar at every 20 min interval for 60 min hydrolysis of three pretreated water hyacinth samples (Sample 2, 4, and 11B). Given a specific target of sugar yield, for

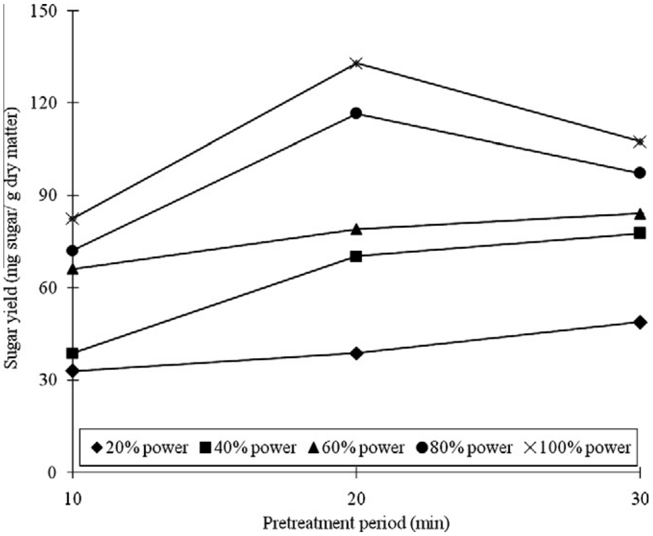

Fig. 2. Hydrolysis response (g sugar/mg dry matter) of water hyacinth samples treated at different ultrasonicator percent power and irradiation period.

example 100 mg sugar/g dry matter, the required hydrolysis time depends on type of pretreatment imposed on the feedstock. For dried samples, 55 min of hydrolysis is required to achieve the target. For ultrasonication pretreatment (20 min at 100% amplitude size), the required hydrolysis time had reduced to 44 min. For dried and powdered samples, the time taken to produce similar amount of sugar is only 39 min. Without pretreatment applied to the samples, a total 60 min of hydrolysis had only yielded 24.69 mg sugar/ g dry matter, which is very low in comparison with those obtained from pretreated samples. Similar findings on the study of hydrolysis rate and time found that the reduction of hydrolysis time is closely related to lower crystallinity level of physically pretreated biomass (Zhu et al., 2008). Higher sugar yield may be achieved from raw sample by extending the hydrolysis time but it is commonly unfavorable since the sugars may be degraded (Balat et al., 2008).

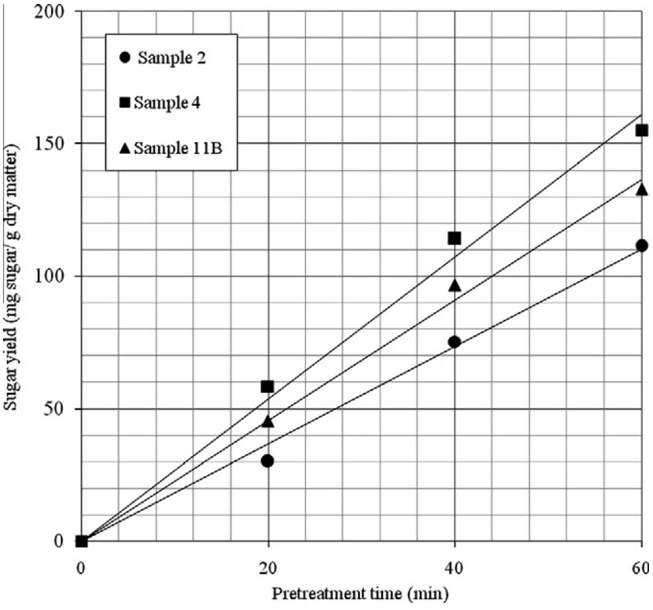

Fig. 3. Sugar release corresponds to hydrolysis time of pretreated water hyacinth samples.

3.3. Effect of pretreatment on plant morphology

Water hyacinth samples from before and after pretreatment processes were viewed under light microscope to detect changes on their morphologies. Good morphological comparisons of water hyacinth samples were obtained at 1000× magnification. In the specimen of untreated water hyacinth (Sample 1), it can be observed that the organelles are randomly positioned within the cells' cytoplasm. The cell walls are intact and not damaged. After being steamed at 121 ± 3 °C for 30 min, the cells were seen to be swollen and overlapped with the adjacent cells. Some cells were burst resulting from overswelling, induced by the constant heat supply from the steaming process. As the cells collapsed, the biomass structure had weakened and the cells' content (moisture, organelles) being removed. Similar observation was also found on boiled samples where cells are swollen and burst.

Ultrasonication pretreatment also caused the cell wall to break but no swelling was found as in steamed sample. The breaking of cell wall is due to the applied ultrasonic waves that generate micro bubbles which eventually collapse and exert substantial forces on the substrate that was suspended in the medium (Chukwumah et al., 2009). The resulting structure alteration in boiling, steaming and ultrasonication pretreatment had caused the lignocellulosic components in the water hyacinth biomass to be liberated and became more accessible for exploitation in the subsequent process. For this reason, sugar yield from acid hydrolysis of steamed, boiled and ultrasonicated sample (Sample 4x, 5x, 7x–11x) was found to be higher compared to untreated sample (Sample 1).

In dried sample (Sample 2), wrinkles appeared on the surface of the specimen due to the shrinkage of the cell as the moisture evaporated. The organelles (seen as black dots) were also shrunk due to moisture loss. Moisture removal benefits the processing of biomass by increasing the porosity level of the material and collapsing the structure (Karathanos et al., 1996) and in acid hydrolysis; the moisture removal will avoid the acid being diluted as it permeates through the substrate. This is proven when dried sample (Sample 2) has produced higher sugar production in acid hydrolysis against wet samples (Sample 1).

These morphology inspections have discovered alteration on water hyacinth structure resulting from pretreatment processes. The investigation was continued by examining the samples under thermal analysis.

3.4. Thermal analysis

The thermogravimetric (TG) and first derivative thermogravimetric (DTG) curves for pyrolysis of pretreated water hyacinth samples (Sample 1, 5A, 6A, and 11B) are presented in Fig. 4a–d, respectively. A slow heating rate (10 °C/min) had provided clear separation between stages in the thermal analysis as suggested by Sricharoenchaikul and Atong (2009). Four major stages in thermal degradation of water hyacinth samples were marked accordingly in Fig. 4a, (1) moisture evaporation, (2) degradation of hemicellulose and cellulose, (3) degradation of lignin and (4) formation of pyrolytic char in. The first stage starts from 25 until 200 °C, with two peaks detected at 50 and 165 °C. Weight loss at this stage is relevant to evaporation of volatile matters and moisture residual from samples as the system heats up (Girisuta et al., 2008).

Decomposition of hemicellulose and cellulose is the major stage in biomass pyrolysis that initiated at 200 °C and ended at 350 °C, and was anticipated to have the most weight loss (Negro et al., 2003). In TG curves for Sample 1 and Sample 6A, there were two peaks detected at 265 and 325 °C at this stage. Peaks at a defined range in pyrolysis thermogram refer to maximum decomposition rate of a component in the sample. Peak at lower temperature

(265 °C) in this region represents the maximum decomposition of hemicellulose while peak the higher temperature (325 °C) is the maximum for cellulose degradation (Chen and Kuo, 2010). However, the bimodal peaks were not detected in the DTG curves of Sample 5A and Sample 11B. Only one peak was detected at 325 °C and the hemicellulose peak became a shoulder in the curve. Absence of double peaks might relate to the liberation of hemicellulose and cellulose from the biomass structure during the pretreatment processes. The digestibility of hemicellulose and cellulose is measured by the weight loss of these components at their respective region in TG curve. In untreated sample (Sample 1), the total weight loss is 36%. Higher consumption was obtained in pretreated samples – Sample 6A (39%), Sample 5A (44%) and Sample 11B (49%). Higher digestibility of pretreated sample corresponds to their enhanced sugar production during dilute acid hydrolysis (Table 3) compared to untreated sample. Another study shows that ultrasonication-assisted preparation of biomass had reduced the lignin association with holocellulose and improved the subsequent processes (Sun and Tomkinson, 2002).

Further decomposition at 350 until 470 °C is attributed to lignin degradation. However, in single component pyrolysis, other researchers found that decomposition of lignin occurs gradually at a very low rate during the whole temperature range (Haykiri-Acma et al., 2010). This phenomenon is closely related to the lignin's complex structure (Yang et al., 2007). The stage beyond 500 °C is related to formation of pyrolytic char from lignin, some inorganic, low crystalline hemicellulose and cellulose (Haykiri-Acma et al., 2010). There were notable peaks detected on the DTG curves of all samples at this stage and it has been suggested that these peaks were associated to some component that are reactive at a temperature above 500 °C (Chen and Kuo, 2010). Finally, the yield of char from untreated and treated samples was also found to be different. Pyrolysis of untreated samples had yielded char of 33% from sample weight while ultrasonicated, boiled and steamed samples have final char yield of 25%, 27% and 25%, respectively. Lower char yield at the end of pyrolysis cycle is another indicator on substrate's digestibility, of how much the substrate has been utilized during the process.

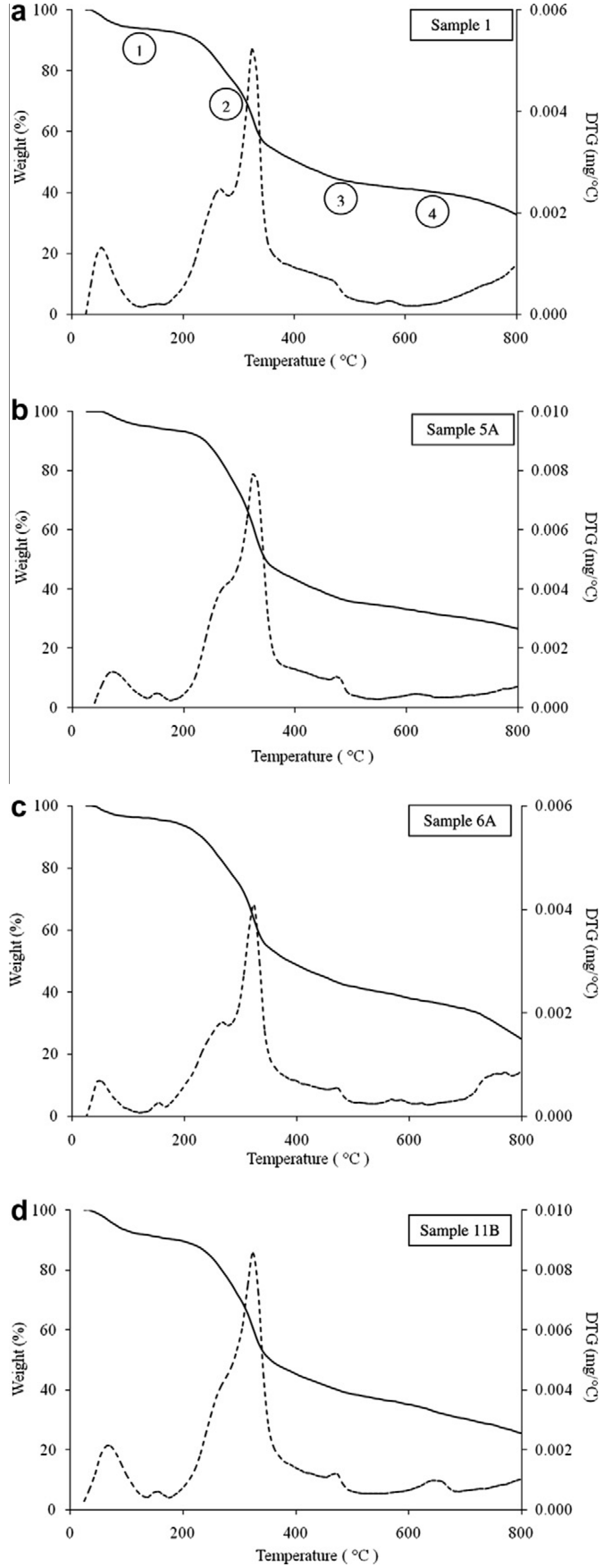

Fig. 4. Thermogravimetric (TG) and differential thermogravimetric (DTG) curve for pyrolysis of (a) untreated (Sample 1); (b) boiled (Sample 5A); (c) steamed (Sample 6A); and (d) ultrasonicated (Sample 11B) water hyacinth sample.

4. Conclusion

The presented results had demonstrated the ability of physical pretreatment on water hyacinth for improving the yield of sugar and processing time in dilute acid hydrolysis. The best pretreatment method concluded in this study was the combination of drying and grinding, with yield of 155.13 mg sugar/g dry matter, about 6-fold higher than raw feedstock (24.69 mg sugar/g dry matter). Morphology inspections and thermal analysis had revealed disruptions on the water hyacinth structure which explained the enhancement of hydrolysis process. Future works may focus on optimization of pretreatment methods and economic evaluation for selecting feasible pretreatment method.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.biortech.2011.02.001.

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